

**TRANSLATOR'S DECLARATION**

I, Nobue Kanaka, state:

that I am thoroughly familiar with both the Japanese and English languages; and

that the attached document represents a true English translation of the rough draft specification entitled "Outline of New Patent Application".

June 26, 2003  
Date

Nobue Kanaka  
Translator

## Outline of New Patent Application

### 1. Title of the invention (provisional):

A method for the formation of a resist hole pattern

### 2. Claims (proposed):

(1) A method for the formation of a resist hole pattern characterized in that, in a method for forming a resist hole pattern which comprises:

(I) a step of coating the surface of a substrate with a positive-working resist composition followed by drying to form a resist film;

(II) a step of exposing the aforementioned resist film to light through a halftone phase-shift mask;

(III) a step of subjecting the resist film after exposure to light to a heat treatment; then,

(IV) a step of alkali development of said resist film to form a resist hole pattern; and

(V) a step of effecting flow of the resist pattern by heating thereby to render the size of the resist pattern smaller than the size after the development,

the aforementioned positive-working resist composition is a chemical amplification positive-working resist composition comprising (A) a substrate resinous compound consisting of polymers comprising (a-1) units substituted by acid-dissociable groups for hydrogen atoms of phenolic hydroxyl groups or carboxyl groups and (a-2) hydroxystyrene units, (B) a compound generating an acid by irradiation with a radiation, (C) a divinyl ether compound crosslinkable with the component (A) by heating before exposure to light for formation of a resist film, and (D) an organic amine.

(2) The method for the formation of a resist hole pattern described in Claim 1 in which the amounts of the components (C) and (D) are, per 100 parts by mass of (A), from 0.1 to 25 parts by mass of (C) and from 0.01 to 1 part by mass of (D),

respectively.

(3) The method for the formation of a resist hole pattern described in Claims 1 or 2 in which a resist hole pattern is formed with the dose of size change per unit temperature being not exceeding 10 nm/°C.

(4) The method for the formation of a resist hole pattern described in either one of Claims 1 to 3 in which an inorganic or organic antireflection film is provided so as to intervene between the substrate and the resist film.

### 3. Prior art technology and object of the present invention

The present invention relates to a method for forming a resist hole pattern using a halftone phase-shift mask and by thermal flow process.

The phase-shift method is known as the method in which a thin film (shifter) of a transparent material to shift the phase of light is formed on localized areas of a mask and the interference of the phase-shifted light by passing through the shifter and the light not passing through the shifter without a phase shift is utilized to improve the patterning resolution ("Lithography technology towards the G bit-era", published by Kabushiki Kaisha Riaraizu, Section 3, Paragraph 3 "Phase-shift method"). Among various phase-shift masks proposed heretofore, the halftone phase-shift mask is leading in the application for real devices (the same literature, Section 5, Paragraph 2 "Phase-shift mask").

This method for resist hole pattern formation using the halftone phase-shift mask has an advantage of increasing pattern resolution and focusing depth characteristics but has a problem that, as pointed out in the publication of Patent Kokai 11-15151, hollow dimples occur around the resist hole due to the occurrence of a subpattern of the light called sidelobe around the main pattern.

On the other hand, there is a process, which is called the thermal flow process in recent years, by which fineness of

semiconductor devices is further increasing, wherein after a resist pattern is formed via usual lithography of exposure to light, heating after exposure to light and an alkaline development, the resist pattern is subjected to flow by heating to form a resist pattern finer in the size of the resist pattern after development (Patent Kokai 2000-188250 publication).

The thermal flow process has an advantage that the increase in fineness can be accomplished by using existing materials for resist so that increase in fineness can be performed without expensive investment. It is, however, necessary to strictly control the amount of size change of the resist pattern at the temperature when a resist pattern after development is subjected to flow by heating to decrease the size of the resist pattern. Among the chemical-amplification resists having been proposed, there cannot be obtained one which is satisfactory for the characteristics in such a thermal flow process.

Much less, in the method for resist hole pattern formation using the halftone phase-shift mask, there is no report of a chemical-amplification resist capable of suppressing such dimples and controlling the amount of change in a resist pattern.

Accordingly, in the present invention, the object is to provide a method for the formation of a resist hole pattern capable of suppressing occurrence of dimples in the halftone phase-shift mask process and, in addition, by developing a positive-working resist composition suitable for the thermal flow process with small amount of size change of a resist pattern per temperature.

#### 4. Means to accomplish the object

The object of the present invention was accomplished by using a chemical amplification positive-working resist composition comprising:

- (A) a substrate resinous ingredient consisting of polymers comprising (a-1) units substituted by acid-dissociable groups for hydrogen atoms of phenolic hydroxyl groups or carboxyl groups and (a-2) hydroxystyrene units;
- (B) a compound generating an acid by irradiation with a radiation;
- (C) a divinyl ether compound crosslinkable with the component (A) by heating before exposure to light for formation of a resist layer; and
- (D) an organic amine.

(The object was accomplished by excluding the carboxylic acid component from those of the invention in Patent Application 2000-264529.)

#### 5. Description of constituting ingredients

Detailed description is omitted since it is same as in the specification of Patent Application 2000-264529 of our company except omission of the carboxylic acid component.

By using the components (C) and (D) in combination but excepting a carboxylic acid component, excellent effect is obtained that occurrence of dimples can be suppressed and that the amount of size change of a resist pattern per temperature is small in the thermal flow process. It is presumed that this is due to the suppression of dissociation of acid-dissociable solubility-reducing groups on the resist surface.

Incidentally, the amount of size change of a resist pattern in the inventive method is not exceeding 15 nm/°C or smaller, preferably, 10 nm/°C or smaller or, more preferably, 5 nm/°C or smaller.

The effective compounding amounts of the components (C) and (D) are, per 100 parts by mass of (A), from 0.1 to 25 parts by mass or, preferably, from 1 to 15 parts by mass of (C) and from 0.01 to 1 part by mass or, preferably, from 0.05 to 0.7 part by mass of (D), respectively.  
Regarding the component (A)

Particularly, followings are given as examples.

- polyhydroxystyrene substituted for the hydrogen atoms of 10 to 60% by mole of the hydroxyl groups thereof by 1-ethoxyethyl groups;
- polyhydroxystyrene substituted for the hydrogen atoms of 10 to 60% by mole of the hydroxyl groups thereof by *tert*-butoxycarbonyl groups;
- polyhydroxystyrene substituted for the hydrogen atoms of 10 to 60% by mole of the hydroxyl groups thereof by *tert*-butoxycarbonylmethyl groups;
- polyhydroxystyrene substituted for the hydrogen atoms of 10 to 60% by mole of the hydroxyl groups thereof by *tert*-butyl groups
- polyhydroxystyrene substituted for the hydrogen atoms of 10 to 60% by mole of the hydroxyl groups thereof by tetrahydropyranyl groups;
- polyhydroxystyrene substituted for the hydrogen atoms of 10 to 60% by mole of the hydroxyl groups thereof by tetrafranyl groups and the like are given as examples.
- copolymer consisting of from 10 to 49% of hydroxy-styrene units substituted for the hydrogen atoms of the hydroxyl groups by *tert*-butoxycarbonyl groups, from 10 to 49% of hydroxystyrene units substituted for the hydrogen atoms of the hydroxyl groups by 1-ethoxyethyl groups and from 2 to 80% of hydroxystyrene units
- copolymer consisting of from 10 to 49% of hydroxy-styrene units substituted for the hydrogen atoms of the hydroxyl groups by *tert*-butyl groups, from 10 to 49% of hydroxystyrene units substituted for the hydrogen atoms of the hydroxyl groups by 1-ethoxyethyl groups and from 2 to 80% of hydroxystyrene units
- copolymer consisting of from 10 to 49% of hydroxy-styrene units substituted for the hydrogen atoms of the hydroxyl

groups by tetrahydropyranyl groups, from 10 to 49% of hydroxystyrene units substituted for the hydrogen atoms of the hydroxyl groups by 1-ethoxyethyl groups and from 2 to 80% of hydroxystyrene units

- polymers containing from 2 to 30% by moles of (meth)acrylic acid ester units substituted for the carboxyl hydrogen atoms by *tert*-butyl groups, from 40 to 80% by moles of hydroxystyrene units and from 10 to 40% by moles of styrene units

- polymers containing from 2 to 30% by moles of (meth)acrylic acid ester units substituted for the carboxyl hydrogen atoms by 1-ethylcyclohexyl groups, from 40 to 80% by moles of hydroxystyrene units and from 10 to 40% by moles of styrene units

The weight average molecular weight of such a polymer is usually from 2000 to 50000 or, preferably, from 5000 to 25000. Regarding the component(B)

Preferable compounds generating an acid by irradiation with a radiation include diazomethane-based acid-generating compounds and onium salts with alkylsulfonic acid of which the alkyl group has 1 to 15 carbon atoms as the anion.

Regarding the component (C)

Particular examples include:

ethyleneglycol divinyl ether,  
triethyleneglycol divinyl ether,  
1,3-butanediol divinyl ether,  
tetramethyleneglycol divinyl ether,  
neopentylglycol divinyl ether,  
trimethylolpropane trivinyl ether,  
trimethylolethane trivinyl ether,  
hexanediol divinyl ether,  
1,4-cyclohexanediol divinyl ether,  
tetraethyleneglycol divinyl ether,  
pentaerythritol divinyl ether,  
pentaerythritol trivinyl ether,  
cyclohexanedimethanol divinyl ether and the like.

Regarding the component (D)

Alkanol amines such as alkanol amines such as diethanolamine, triethanolamine and tributanolamine and the like are preferable because of their ability of suppressing dimples satisfactorily.

The method for the formation of a resist hole pattern of the present invention comprises:

- (I) a step of coating the surface of a substrate with the positive-working resist composition followed by drying to form a resist film;
- (II) a step of exposing the aforementioned resist film to light through a halftone phase-shift mask;
- (III) a step of subjecting the resist film after exposure to light to a heat treatment; then,
- (IV) a step of alkali development of said resist film to form a resist hole pattern; and
- (V) a step of effecting flow of the resist pattern by heating thereby to render the size of the resist pattern smaller than the size immediately after the development.

Each of these steps can be the step usually undertaken. In general, the method of spin coating is used for coating in step (I) and the drying temperature is from 80 to 150 °C for 30 to 120 seconds. The heat treatment in step (III) is conducted on a hot plate at from 90 to 150 °C for 30 to 120 seconds. The heat treatment in step (V) is conducted on a hot plate at from 110 to 180 °C for 30 to 180 seconds.

In the present invention, it is preferable to provide an inorganic or organic antireflection film so as to intervene between the substrate and the photoresist film because of its effect of improving the pattern resolution further and suppressing the substrate dependency which is a phenomenon that the profile of the resist pattern is adversely affected as a result of the influence of a variety of thin films (SiN, TiN, BPSG and the like) provided on the substrate.



The organic antireflection film is exemplified by SWK Series ones (produced by Tokyo Ohka Kogyo Co.), DUV Series ones (produced by Brewer Science Co.) and AR Series ones (produced by Shipley Co.) and the like and the inorganic antireflection film is exemplified by SiON and the like.

## 6. Examples and Comparative Examples

Incidentally, the various properties of the positive-working resist compositions were determined in the following manner.

### (1) Sensitivity

A silicon wafer provided with an anti-reflection film of SWK-EX2 (a product by Tokyo Ohka Kogyo Co.) having a film thickness of 0.12  $\mu\text{m}$  was coated by using a spinner with the prepared resist composition and the same was dried on a hot plate at 90 °C for 90 seconds to obtain a resist film having a film thickness of 0.5  $\mu\text{m}$ . This film was subjected to light-exposure with a KrF excimer laser through a half-tone phase shift mask by using a minifying projection light-exposure machine FPA-3000EX3 (manufactured by Canon Co.) with successive increments of dose each by 1  $\text{mJ}/\text{cm}^2$  followed by PEB (POST EXPOSURE BAKE) at 110 °C for 90 seconds and development at 23 °C taking 60 seconds with a 2.38% by weight aqueous solution of tetramethylammonium hydroxide followed by water rinse for 30 seconds and drying to determine the minimum light-exposure time taken as the sensitivity in the unit of  $\text{mJ}/\text{cm}^2$  (quantity of energy) by which the film thickness in the light-exposed areas after development was 0.

### (2) Profile of resist pattern

A resist hole pattern of 0.25  $\mu\text{m}$  diameter obtained by the same procedure as in (1) above was observed by a SEM (scanning electron microscope) and evaluated for the profile thereof and occurrence of dimples. Evaluation was made as A for the hole pattern straight down to the substrate bottom and B for the profile narrowing toward the substrate bottom.

(3) Pattern resolution

The critical resolution was examined on the resist hole pattern obtained in the same procedure as in (1) above.

(4) Thermal flow behavior

The resist hole pattern of 0.20  $\mu\text{m}$  diameter obtained in the same procedure as in (1) above was heated to be reduced down to 0.15  $\mu\text{m}$ . The thus formed 0.15  $\mu\text{m}$  resist pattern was evaluated for the flow rate (the amount of size change of the resist pattern per  $^{\circ}\text{C}$ ) expressed as  $\text{nm}/^{\circ}\text{C}$  to give  $\odot$  for 5  $\text{nm}/^{\circ}\text{C}$  or smaller,  $\bigcirc$  for exceeding 5 but not exceeding 15  $\text{nm}/^{\circ}\text{C}$  and  $\times$  for exceeding 15  $\text{nm}/^{\circ}\text{C}$ .

Example 1.

A positive-working resist composition was prepared by dissolving, in 490 parts by weight of propyleneglycol monomethyl ether acetate,

(A1) 75 parts by weight of a polyhydroxystyrene having a weight-average molecular weight of 10000 with a degree of dispersion of 1.2, of which 39% by moles of the hydroxyl groups were substituted for the hydrogen atoms by 1-ethoxyethyl groups,

(A2) 25 parts by weight of a polyhydroxystyrene having a weight-average molecular weight of 10000 with a degree of dispersion of 1.2, of which 36% by moles of the hydroxyl groups were substituted for the hydrogen atoms by tert-butoxycarbonyl groups,

5 parts by weight of bis(cyclohexylsulfonyl) diazomethane,

5 parts by weight of cyclohexane dimethanol divinyl ether,

0.2 part by weight of triethylamine, and

0.05 part by weight of a fluorosilicone-based surface active agent,

followed by filtration thereof through a membrane filter of 0.2  $\mu\text{m}$  pore diameter.

The results of the evaluation of this for the properties

described above are shown in Table 1.

#### Example 2.

A positive-working resist composition was prepared in the same manner as in Example 1 except that, in Example 1, the component (A2) was not used and the component (A1) was taken in 100 parts by weight and then evaluation of the properties described above was made. The results thereof are shown in Table 1.

#### Example 3.

A positive-working resist composition was prepared in the same manner as in Example 1 excepting, in Example 1, replacement of the components (A1) and (A2) with the followings and was subjected to evaluation of the properties described above. The results are shown in Table 1.

(A1) 70 parts by weight of a polyhydroxystyrene having a weight-average molecular weight of 10000 with a degree of dispersion of 1.2, of which 39% by moles of the hydroxyl groups were substituted for the hydrogen atoms by 1-ethoxyethyl groups

(A3) 30 parts by weight of a polyhydroxystyrene having a weight-average molecular weight of 10000 with a degree of dispersion of 1.2, of which 30% by moles of the hydroxyl groups were substituted for the hydrogen atoms by tetrahydropyranyl groups

#### Example 4.

A positive-working resist composition was prepared in the same manner as in Example 1 excepting, in Example 1, the replacement of the components (A1) and (A2) with the followings and was subjected to evaluation of the properties described above. The results are summarized in Table 1.

(A1) 75 parts by weight of a polyhydroxystyrene having a weight-average molecular weight of 10000 with a degree of

dispersion of 1.2, of which 39% by moles of the hydroxyl groups were substituted for the hydrogen atoms by 1-ethoxyethyl groups

(A3) 25 parts by weight of a polyhydroxystyrene having a weight-average molecular weight of 10000 with a degree of dispersion of 1.2, of which 30% by moles of the hydroxyl groups were substituted for the hydrogen atoms by *tert*-butyl groups

#### Example 5.

A positive-working resist composition was prepared in the same manner as in Example 1 excepting, in Example 1, the replacement of the components (A1) and (A2) with the followings and was subjected to evaluation of the properties described above. The results are summarized in Table 1.

60 parts by weight of a copolymer having a weight-average molecular weight of 10000 and consisting of 65% by moles of hydroxystyrene, 20% by moles of styrene and 15% by moles of *tert*-butyl acrylate

40 parts by weight of a copolymer having a weight-average molecular weight of 10000 and consisting of 75% by moles of hydroxystyrene, 20% by moles of styrene and 5% by moles of *tert*-butyl acrylate.

#### Example 6.

A positive-working resist composition was prepared in the same manner as in Example 1 excepting, in Example 1, the replacement of trimethanol amine with the same amount of triethylbutyl amine and change of the amount of cyclohexane dimethanol divinyl ether to 2.5 parts by mass and was subjected to evaluation of the properties described above. The results are summarized in Table 1.

#### Comparative Example 1 (with an carboxylic acid).

A positive-working resist composition was prepared in the

same manner as in Example 1 excepting, in Example 1, addition of 0.2 part by mass of salicylic acid and was subjected to evaluation of the properties described above. The results are summarized in Table 1.

Comparative Example 2 (without a divinyl ether).

A positive-working resist composition was prepared in the same manner as in Example 1 excepting, in Example 1, omission of cyclohexane dimethanol divinyl ether and was subjected to evaluation of the properties described above. The results are summarized in Table 1.

T a b l e 1

Example/ Comparative Example	Sensi- tivity (mJ/cm <sup>2</sup> )	Resist pattern profile	Dimples	Resolu- tion (μm)	Thermal flow
Example 1	40	A	no	0.18	◎
Example 2	35	A	no	0.17	○
Example 3	42	A	no	0.18	◎
Example 4	44	A	no	0.18	◎
Example 5	30	A	no	0.18	◎
Example 6	37	B	a little but accept- able	0.18	○
Comparative Example 1	42	A	yes	0.18	◎
Comparative Example 2	35	A	no	0.18	×